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Solubility of N_2O in and Density, Viscosity, and Surface Tension of Aqueous Piperazine Solutions

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The physical solubility of N_2O in and the density and viscosity of aqueous piperazine solutions have been measured over a temperature range of (293.15 to 323.15) K for piperazine concentrations ranging from about (0.6 to 1.8) kmol·m^{-3}. Furthermore, the present study contains experimental surface tension data of aqueous piperazine solutions at temperatures of (293 and 313) K and at concentrations of (0.5, 1.0, and 1.5) kmol·m^{-3} piperazine in water.

Introduction

The removal of acid gases, such as CO_2 and H_2S, from industrial gases is frequently carried out by an absorption−desorption technology, using (aqueous) solutions containing alkanolamines as solvents.[1] One industrially applied solvent is the piperazine (PZ) activated aqueous *N*-methyldiethanolamine (MDEA) solution.[2] Such a blend of an activator (usually a primary or secondary amine) with a tertiary amine combines the relatively high rate of reaction of the former with CO_2 with the lower reaction heat of the latter with CO_2, thereby gaining higher rates of absorption in the absorption column while maintaining a low energy of regeneration in the stripper section.

An optimal design and operation of absorption and desorption columns requires detailed knowledge concerning (among other things) the mass transfer rate of carbon dioxide into the absorption liquid, which in turn is to a large extent determined by the kinetic rates of both the activator (PZ) and the tertiary amine (MDEA) with CO_2. And, while the kinetics of MDEA with CO_2 have been studied extensively in the past,[3] only two publications have dealt with the (independent) measurement of the reaction rate of PZ with CO_2.[4,5] As the kinetics are typically derived from mass transfer experiments, a correct interpretation of these experiments requires the knowledge of the physical solubility and diffusivity of CO_2 in aqueous piperazine solutions. Unfortunately, it is not possible to determine these properties directly due to the chemical reactions between CO_2 and (aqueous) piperazine.

In the literature,[3,6−8] therefore, it is suggested to apply the "N_2O analogy" to estimate both of the aforementioned physicochemical properties. This seems reasonable since N_2O resembles CO_2 in configuration, molecular volume, and electronic structure; moreover, it is a non-reactive gas.

Recently, research[9] has also focused on the application of microporous membranes as a gas−liquid contactor, which (within certain operating conditions) could offer some advantages over conventional contactors, such as ease of scale-up, higher interfacial area per unit volume, and the possibility to vary mass transfer coefficients and interfacial area independently. One major disadvantage when working with organic solvents is the possibility of wetting of the membrane, which means that the absorption liquid penetrates the membrane pores, thereby imposing an additional (very large) mass transfer resistance. The minimum pressure (ΔP_{LY}) required for the liquid to penetrate into the membrane pores (with pore diameter d_{pore}) is, according to the Laplace−Young equation, linearly dependent on its surface tension (γ_L):

$$\Delta P_{LY} = -\frac{4\gamma_L \cos\theta}{d_{pore}} \quad (1)$$

Also for conventional gas−liquid contactors such as absorption columns, the surface tension of a liquid is a nontrivial property since it affects important design parameters, such as hydrodynamics, volumetric mass transfer coefficient, and gas holdup.[10]

The present work reports densities, viscosities, and N_2O solubilities at temperatures in the range (293.15 to 323.15) K and surface tensions at (293 and 313) K. The piperazine concentration range studied was about (0.6 to 1.8) kmol·m^{-3} in the density, viscosity, and N_2O solubility measurements, while the surface tension was measured at piperazine concentrations of (0.5, 1.0, and 1.5) kmol·m^{-3}.

Experimental Section

Solutions of PZ were prepared by dissolving a known amount of piperazine (purity 99 %, Aldrich) in double-distilled water. The actual concentration of the prepared solution was measured (at T = 293 K) by means of a volumetric titration with a 1.0 mol·L^{-1} solution of HCl. The experimentally determined piperazine concentrations were accurate to within 0.5 %. The nitrous oxide (purity 99.5 %) used in the solubility experiments was obtained from Hoekloos.

Density and Viscosity. The density was determined with a commercial density meter (DMA 58, Anton Paar GmbH), in which the temperature could be controlled within ± 0.05 K. The viscosity was measured using a PSL Ubbelohde viscometer (type ASTM-IP, capillary 0C), submerged in a thermostatbath for temperature control (within ±0.1 K).

Solubility. The physical solubility of N_2O was measured in a thermostated reactor (volume ≈ 2 L), equipped with a

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Table 1. Distribution Coefficient of N_2O in Water (m) at Various Temperatures

T/K	m	T/K	m
293.15	0.674	313.15	0.428
298.15	0.592	323.15	0.366
303.15	0.524		

gas inducing impeller, connected to a calibrated gas vessel. Both reactor and gas supply vessel were provided with a temperature and pressure indicator. A known amount of PZ solution was transferred to the reactor and allowed to reach the desired temperature, after which the liquid was degassed by applying vacuum for a short period. Then, the gas supply vessel was filled with pure N_2O, and the initial pressure in this vessel was recorded. Next, a sufficient amount of N_2O was fed from the gas supply vessel to the reactor. Subsequently, the valve between the gas supply vessel and the reactor was closed, and the final pressure in the gas supply vessel was recorded. After this, the agitator in the reactor was switched on, the contents of the reactor was allowed to reach equilibrium (which was reached when the reactor pressure remained constant), and the equilibrium pressure and the corresponding temperature in the reactor were recorded. Subsequently, the temperature in the reactor was adjusted to a different desired temperature using the thermostat bath, and again the solution was allowed to reach equilibrium. Following this method, a series of experimental solubilities at different temperatures could be obtained using one solution of certain piperazine concentration.

The distribution coefficient, defined in this work as the ratio between the equilibrium concentrations in the liquid and the gas phase, at each temperature was calculated using the difference between the initial and final pressure in the gas supply vessel, the equilibrium pressure, and the vapor pressure of the lean solution at the corresponding temperature, according to eqs 2, 3, and 4:

$$\Delta n_{N_2O} = \frac{\Delta P_{GV} V_{GV}}{R T_{GV}} \tag{2}$$

$$P_0(T) = \frac{\Delta n_{N_2O} R T}{V_{gas}} + P_{vap}(T) \tag{3}$$

$$m(T) = \left(\frac{C^{liq}_{N_2O}(T)}{C^{gas}_{N_2O}(T)}\right)_{eq} = \frac{P_0(T) - P_{eq}(T)}{P_{eq}(T) - P_{vap}(T)} \frac{V_{gas}}{V_{liq}} \tag{4}$$

The vapor pressure in the reactor was calculated from the vapor pressure of pure water[11] thereby assuming Raoult's law to correct for the piperazine content:

$$P_{vap}(T) = x_{H_2O} \cdot P^{pure}_{H_2O}(T) \tag{5}$$

The error introduced with this assumption is expected to be minimal, considering the concentration range studied ($x_{H_2O} > 0.96$).

Experimental procedure and accuracy were verified by measuring the solubility of N_2O in water. Results are shown in Table 1 and Figure 1. From Figure 1 it is clearly shown that the measured solubilities are well in line with experimental data taken from various literature sources.[5,12−14]

Surface Tension. Surface tension measurements were carried out with a Krüss K9 tensiometer, using the Wilhelmy plate method. Measurements were performed at temperatures of (293 ± 1) and (313 ± 1) K. The maximum experimental uncertainty caused by these temperature changes amounts to 0.3 mN·m^{-1} (for water).

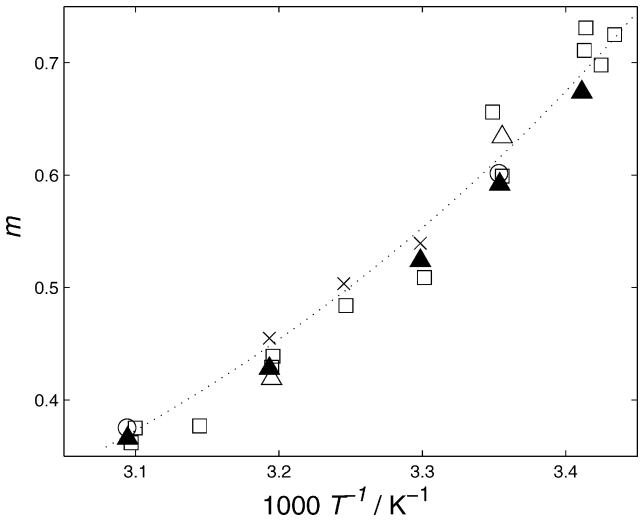

Figure 1. Distribution coefficient of N_2O in water (m) as a function of temperature. ▲, this work; ×, Sun et al.;[5] △, Duda and Vrentas;[12] □, Versteeg and van Swaaij,[13] ○, Xu et al.[14] Dashed line represents the correlation for N_2O solubility in water as proposed by Versteeg and van Swaaij.[13]

Table 2. Densitiy (ρ) and Viscosity (η) of Aqueous Piperazine Solutions

	C_{PZ}/kmol·m^{-3}	ρ/kg·m^{-3}	η/mPa·s^{-1}
T = 293.15 K	0.623	1000.46	1.260
	1.006	1002.49	1.524
	1.490	1005.40	1.865
T = 298.15 K	0.623	999.37	1.105
	1.006	1001.30	1.310
	1.490	1004.11	1.616
	1.686	1005.39	1.803
T = 303.15 K	0.623	997.94	0.980
	1.006	999.79	1.154
	1.490	1002.47	1.402
	1.686	1003.66	1.556
T = 313.15 K	0.623	994.25	0.787
	1.006	996.03	0.922
	1.490	998.49	1.091
	1.686	999.49	1.201
T = 323.15 K	0.623	989.76	0.650
	1.006	991.53	0.747
	1.490	993.86	0.876
	1.686	994.74	0.956

Results and Discussion

Density and Viscosity. The measured values of density and viscosity as a function of concentration and temperature are listed in Table 2. The experimental uncertainty is estimated at 0.01 % (density) and 1 % (viscosity).

Sun et al.[5] also reported density and viscosity data for aqueous piperazine solutions at temperatures of (303.15, 308.15, and 313.15) K and PZ concentrations ranging from (0.23 to 0.92) kmol·m^{-3}. The work of Cullinane[15] contains experimental density and viscosity data at temperatures of (298.15 and 313.15 K) at a concentration range from (0.5 to 1.8) kmol·m^{-3} piperazine in water. A graphical comparison between the three different data sets at (298.15, 303.15, and 313.15) K is shown in Figures 2 and 3.

Figure 2 shows that the presently reported densities are in good agreement with the data by Sun et al.[5] and Cullinane;[15] the deviation between the three data sets is always smaller than 0.25 %. As for the reported viscosities, however, this is not the case, as illustrated in Figure 3.

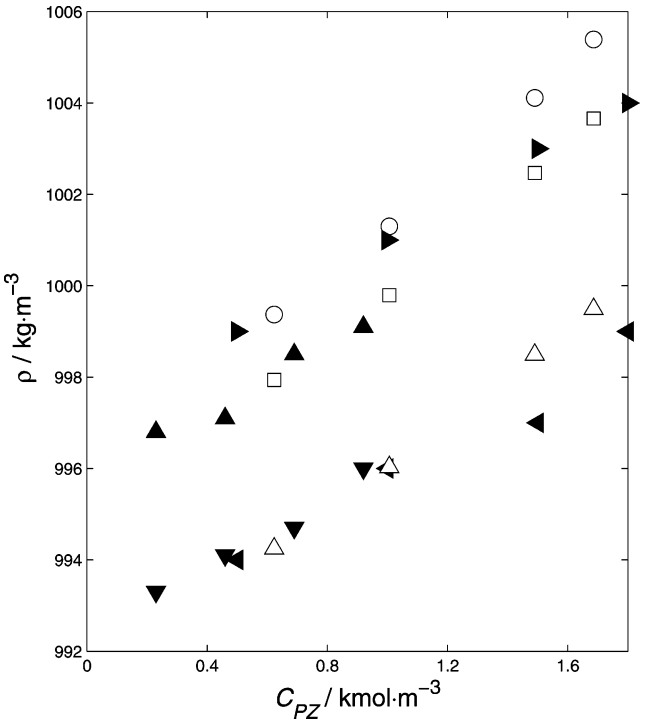

Figure 2. Density of aqueous piperazine solutions (ρ) as a function of PZ concentration. At 298.15 K: ○, this work; solid triangle pointing right, Cullinane.[15] At 303.15 K: □, this work; ▲, Sun et al.[5] At 313.15 K: △, this work; ▼, Sun et al.;[5] solid triangle pointing left, Cullinane.[15]

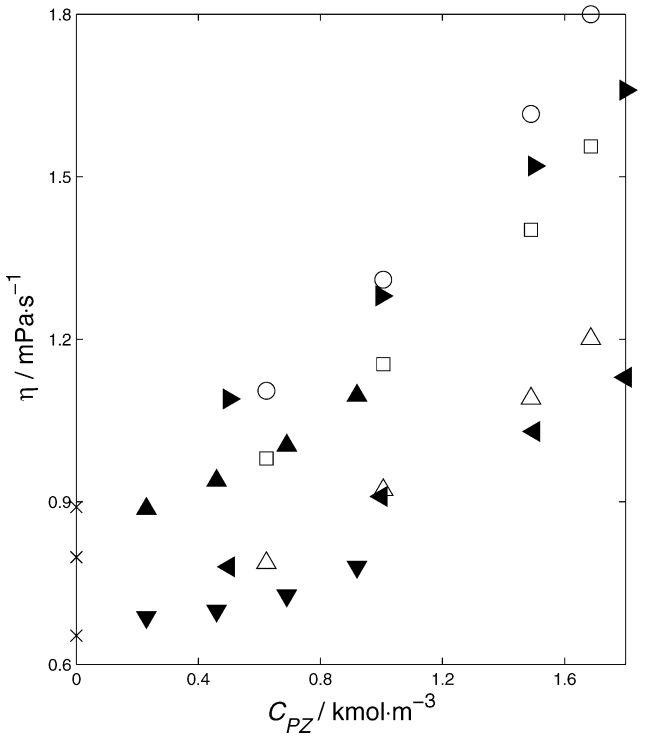

Figure 3. Viscosity of aqueous piperazine solutions (η) as a function of PZ concentration. At 298.15 K: ○, this work; solid triangle pointing right, Cullinane.[15] At 303.15 K: □, this work; ▲, Sun et al.[5] At 313.15 K: △, this work; ▼, Sun et al.;[5] "solid triangle pointing left", Cullinane.[15]

At piperazine concentrations below 1.0 kmol·m^{-3}, there is a good agreement between the present data and the data reported by Cullinane.[15] At higher concentrations, the deviation between the two data sets increases up to about 10 %. The comparison with the experimental data of Sun et al.[5] shows that, while their data at 303.15 K are in good agreement with the present data, their data at 313.15 K are consistently a bit lower than the present data and the data reported by Cullinane.[15]

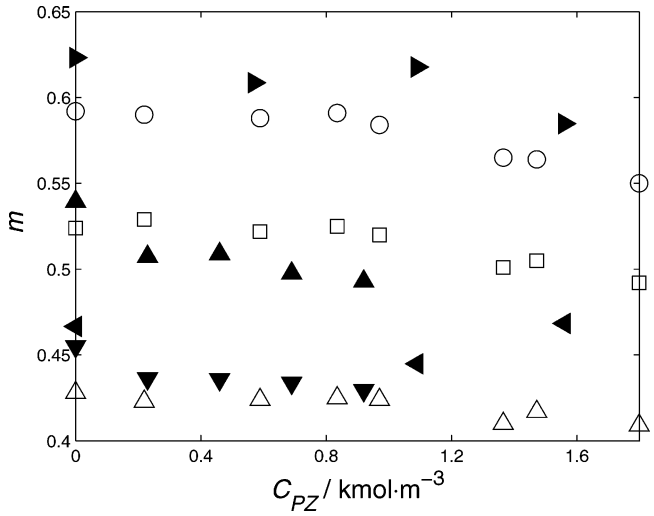

Figure 4. Solubility of N_2O, as the distribution coefficient (m) in aqueous piperazine solutions as a function of PZ concentration. At 298.15 K: ○, this work; solid triangle pointing right, Cullinane.[15] At 303.15 K: □, this work; ▲, Sun et al.[5] At 313.15 K: △, this work; ▼, Sun et al.;[5] "solid triangle pointing left", Cullinane.[15]

Table 3. Solubility of N_2O as the Distribution Coefficient (m) in Aqueous Piperazine Solutions

	T/K =				
C_{PZ}/kmol·m^{-3}	293.15	298.15	303.15	313.15	323.15
0.219	0.678	0.590	0.529	0.423	0.354
0.589	0.669	0.588	0.522	0.424	0.358
0.835	0.674	0.591	0.525	0.425	0.355
0.970	0.662	0.584	0.520	0.424	0.358
1.365	0.637	0.565	0.501	0.410	0.350
1.472	0.637	0.564	0.505	0.417	0.355
1.799		0.550	0.492	0.409	0.351

Pure water viscosity data, taken from Lide,[16] have been included in Figure 3 to compare the trends in all three data series; extrapolation of the data taken at one constant temperature to a zero piperazine concentration should yield the viscosity of (pure) water at that temperature. And although the comparison is a very simple one, it does give an indication that the data sets presented in this work and in the work of Cullinane[15] seem to be more consistent with the limiting case of pure water than the experimental viscosities presented by Sun et al.[5]

N_2O Solubility. The solubility of N_2O in aqueous PZ solutions, quantified in dimensionless form by the distribution coefficient (m) is listed in Table 3. The experimental uncertainty is within 5.0 %.

The solubility data at (298.15, 303.15, and 313.15) K are compared to the corresponding data sets presented by Sun et al.[5] and Cullinane[15] in Figure 4.

The three data sets are reasonably in line with each other; the maximum deviation in the experimental results is found at a temperature of 313.15 K between the experimental data of Cullinane[15] on one hand and the present data and the experimental data of Sun et al.[5] on the other hand. It is noted that an increasing piperazine concentration does have a marginal effect on the N_2O solubility of the solution.

Surface Tension. Surface tensions have been measured for three piperazine concentrations, and the results are listed in Table 4. Each reported value is the average of at

Table 4. Surface Tension (γ) of Aqueous Piperazine Solutions and Aqueous DEA and MDEA Solutions

	C_{am}	w_{am}	γ/mN·m^{-1}		
amine	kmol·m^{-3}	%	$T = 293.15$ K	$T = 313.15$ K	source
none	0	0	72.7	69.8	this work
PZ	0.5	4.3	71.7	68.5	this work
PZ	1.0	8.6	70.1	67.8	this work
PZ	1.5	12.9	69.3	67.6	this work
DEA		10	64.14	61.65	ref 17
DEA		10	63.90	61.74	ref 18
MDEA		10	62.24	58.08	ref 18

least three measurements. Along with the new surface tension data, also literature data on DEA and MDEA solutions are listed.

The addition of a small amount of piperazine to water does not have a pronounced effect on the surface tension of the solution at both (293 and 313) K, whereas the addition of more conventional (alkanol)amines such as DEA and MDEA causes a considerable drop in the surface tension.

Conclusions

This work reports experimentally determined densities, viscosities, and N_2O solubilities of aqueous piperazine solutions at different concentrations and temperatures, thereby expanding the data set already available in the literature. A comparison with the experimental data reported by Sun et al.[5] and Cullinane[15] shows a reasonable to good agreement for all results.

Also, the surface tension of aqueous piperazine solutions was measured at temperatures of (293 and 313) K. It was found that the addition of a small amount of piperazine to water does not have such a pronounced effect on the surface tension as observed for conventional (alkanol)amines such as DEA and MDEA.

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Literature Cited

(1) Kohl, A. L.; Nielsen, R. B. *Gas Purification*, 5th ed.; Gulf Publishing Company: Houston, 1997.
(2) Appl, M.; Wagner, U.; Henrici, H. J.; Kuessnet, K.; Volkamer, F.; Ernst-Neust, N. Removal of CO_2 and/or H_2S and/or COS from gases containing these constituents. U.S. Patent 4336233, 1982.
(3) Versteeg, G. F.; Van Dijck, L. A. J.; van Swaaij, W. P. M. On the kinetics between CO_2 and alkanolamines both in aqueous and non-aqueous solutions. An overview. *Chem. Eng. Commun.* **1996**, *144*, 113−158.
(4) Bishnoi, S.; Rochelle, G. T. Absorption of carbon dioxide into aqueous piperazine: reaction kinetics, mass transfer and solubility. *Chem. Eng. Sci.* **1999**, *55*, 5531−5543.
(5) Sun, W.-C.; Yong, C.-B.; Li, M.-H. Kinetics of the absorption of carbon dioxide into mixed aqueous solutions of 2-amino-2-methyl-1-propanol and piperazine. *Chem. Eng. Sci*. **2005**, *60*, 503−516.
(6) Laddha, S. S.; Diaz, J. M.; Danckwerts, P. V. The N_2O analogy; the solubilities of CO_2 and N_2O in aqueous solutions of organic compounds. *Chem. Eng. Sci.* **1981**, *36*, 229−230.
(7) Sada, E.; Kumazawa, H.; Butt, M. A. Solubilities of gases in aqueous solutions of amine. *J. Chem. Eng. Data* **1977**, *22*, 277−278.
(8) Sada, E.; Kumazawa, H.; Butt, M. A. Solubility and diffusivity of gases in aqueous solutions of amines. *J. Chem. Eng. Data* **1978**, *23*, 161−163.
(9) Kumar, P. S.; Hogendoorn, J. A.; Feron, P. H. M.; Versteeg, G. F. New absorption liquids for the removal of CO_2 from dilute gas streams using membrane contactors. *Chem. Eng. Sci.* **2002**, *57*, 1639−1651.
(10) Deckwer, W.-D. *Bubble Column Reactors*; John Wiley & Sons: Chicester, 1992.
(11) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: Boston, 1987.
(12) Duda, J. F.; Vrentas, J. C. Laminar liquid jet diffusion studies. *AIChE J.* **1968**, *14*, 286−294.
(13) Versteeg, G. F.; van Swaaij, W. P. M. Solubility and diffusivity of acid gases (CO_2 and N_2O) in aqueous alkanolamine solutions. *J. Chem. Eng. Data* **1988**, *33*, 29−34.
(14) Xu, S.; Otto, F. D.; Mather, A. E. Physical properties of aqueous AMP solutions. *J. Chem. Eng. Data* **1991**, *36*, 71−75.
(15) Cullinane, J. T. Thermodynamics and Kinetics of Aqueous Piperazine with Potassium Carbonate for Carbon Dioxide Absorption. Ph.D. Dissertation, University of Texas, Austin, 2005.
(16) Lide, D. R. *Handbook of Chemistry and Physics*, 75th ed.; CRC Press: Boca Raton, FL, 1994.
(17) Aguila-Hernández, J.; Trejo, A.; Gracia-Fadrique, J. Surface tension of aqueous solutions of alkanolamines: single amines, blended amines and systems with nonionic surfactants. *Fluid Phase Equilib.* **2001**, *185*, 165−175.
(18) Rinker, E. B.; Oelschlager, D. W.; Colussi, A. T.; Henry, K. R.; Sandall, O. C. Viscosity, density, and surface tension of binary mixtures of water and *N*-methyldiethanolamine and water and diethanolamine and tertiary mixtures of these amines with water over the temperature range 20−100 °C. *J. Chem. Eng. Data* **1994**, *39*, 392−395.

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